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**REMARKS**

Claims 1-10, 13 and 14 are pending in this application. Claims 11 and 12 have been cancelled herein without prejudice or disclaimer. Claims 1-8 and 10 have been amended and new claims 13 and 14 have been added herein.

The amendments to claims 1-8 and 10 are discussed below. Support for new claims 13 and 14 may be found in the specification on page 5, last paragraph to page 6, first paragraph, and page 14, last paragraph, through page 16, first paragraph.

**Claims 10-12 are objected to because of informalities (Office action paragraph 1).**

The objection is overcome by the amendments to the claims. Claims 11 and 12 have been cancelled without prejudice or disclaimer. Claim 10 has been amended to change the dependency from claim 1 to claim 4.

**Claims 1-12 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite (paragraphs 2-8 of the Office action).**

The rejection is overcome in part by the amendments to the claims and in part traversed.

In paragraph 4 of the Office action, the Examiner indicates that the term "highly weather-resistant" is a relative term that renders the claims indefinite. Applicants note, however, that this term appears in the preamble only, and represents a general name and utility for the invention. As such, this term does not represent a claim limitation and does not constitute a source of

indefiniteness in the claim. Moreover, the present specification indicates on page 11, second paragraph that: "The treated magnet powder remains essentially unchanged in coercive force even when exposed to an atmosphere of 80° C and RH 90% for 24 hours, showing greatly improved resistance to weather." This defines the meaning of "weather resistant" for the purposes of the present claims.

In paragraph 5 of the Office action, the Examiner states that the term "iron-based" renders the claims indefinite. The Examiner similarly comments on the terms "Nd-Fe-B-based" and "Sm-Fe-N-based." The claims have been amended for clarity. The expression "iron-based magnet powder" means a magnet powder comprising iron as an essential component in an amount larger than that of any other components. The term "iron-based" has been deleted and the claim now recites that the powder comprises iron.

The word "based" has been deleted from "Nd-Fe-B-based" and "Sm-Fe-N-based". However, Applicants note that the terms containing "based", such as "iron-based", "Nd-Fe-B-based" and "Sm-Fe-N-based", are well known in the fields of metal alloys, magnets and the like, and frequently used as basic technical terms. Therefore, the meaning of each of these terms is well understood by a person skilled in the art. Applicants enclose herewith copies of several document pages (*Proceedings of the 16<sup>th</sup> International Workshop on Rare-Earth Magnets and Their Applications*, Volume 2, pages 595, 641, 669, 695, 757 and 767) showing that the terms containing "based" are frequently used in these fields.

The expression "Nd-Fe-B-based magnet powder" means a specific type of the above-

mentioned “iron-based magnet powder” in which iron is used in combination with neodymium in the form of an alloy thereof and at least a portion of the iron and/or neodymium is present in the form of a boride.

Further, the expression “Sm-Fe-N-based magnet powder” means another specific type of the above-mentioned “iron-based magnet powder” in which iron is used in combination with samarium in the form of an alloy thereof and at least a portion of the iron and/or samarium is present in the form of a nitride.

In point 6 of the Office action, the Examiner notes that claims 3 and 7 require coating with a zinc film, while claim 1 requires coating with a phosphate film. This rejection is overcome by the amendments to claims 3 and 7. The wording of these claims has been amended to clarify that the particles are coated with a zinc film “before being coated with said phosphate film.”

In point 7 of the Office action, the Examiner indicates that in claims 4 and 8 it is unclear if the Fe refers to the iron in the “iron phosphate” or in the “iron-based magnet powder”. Applicants note that the phrase “comprises iron phosphate in an Fe/rare earth element ratio ...” refers to the Fe in the iron phosphate. See page 9, line 11, of the specification. With regard to the type of ratio, the specification indicates that this is an “elemental ratio”, that is, an atomic or molar ratio. The claims have been amended to clarify this point by reciting “an Fe/rare earth element atomic ratio ....”

In point 8 of the Office action, the Examiner indicates that in claim 5, the phrase “as the main

ingredient” is unclear. The rejection is overcome by the amendment clarifying the recitation of claim

5. The phrase “main ingredient” has been amended to “ingredient present in the largest amount by weight”, as would be generally understood by one of skill in the art.

**Claims 1-3 and 5-7 are rejected under 35 U.S.C. 102(b) as being anticipated by Takahashi (U.S. Patent No. 5,453,137) (Office action point 10).**

The rejection of claims 1-3 and 5-7 is respectfully traversed.

The Examiner refers to Takahashi’s abstract, lines 1-14, in which the reference describes a permanent magnet comprising an acicular iron powder having successively on the surface (1) a coated layer of aluminum phosphate, (2) a diffused layer of rare earth element or a diffused layer of rare earth element.boron or a diffused layer of rare earth element.boron.nitrogen, and (3) a coated layer of aluminum phosphate. The Examiner refers to column 6, line 23, which describes Examples in which an acicular iron particle, coated with aluminum phosphate, has a width of  $0.09\ \mu\text{m}$ , that is, 90 nm. This coated powder is further treated with pulverized rare earth element and boron “to cause diffusion of the rare earth element and boron into the surface layer of the aluminum phosphate coated acicular iron powder” (column 6, lines 28-30). This treated particle is then further treated to form an outer layer of aluminum phosphate.

Applicants respectfully disagree with the Examiner that these Examples of Takahashi anticipate claim 1. First of all, as recited in claim 1, the iron based magnet powder comprises the rare-earth element, and the phosphate film is coated over the particle. However, in Takahashi, the iron particle is coated with aluminum phosphate and then treated to diffuse a rare earth element into

the “surface layer”, that is, the aluminum phosphate coating layer. This structure can be seen in Takahashi’s Fig. 1, as described in column 2, lines 2-7 and 26-44. In particular, the diffused layer of rare earth is designated by reference numeral 3, and this clearly lies above the coated layer of aluminum phosphate shown by reference numeral 1. That is, in Takahashi, the rare earth is not in the particle under the coating, as is required by claim 1.

The Examiner notes that the diffused layer (reference numeral 3) can be Fe.Nd.B.X (column 2, line 6, of Takahashi). However, this alloy is only in the layer designated by reference numeral 3, and therefore this does not meet the structural requirements of claim 1, in which the rare earth element must be in the powder under the phosphate film.

Similar arguments apply to independent claim 5 and dependent claims 2, 3, 6 and 7.

In addition, Applicants respectfully note that the Examiner has not indicated where Takahashi teaches a zinc film as recited in dependent claims 3 and 7. Applicants can find no mention of zinc in Takahashi.

Applicants therefore respectfully submit that claims 1-3 and 5-7 are not anticipated by Takahashi ‘137.

**Claims 1-3 and 5-7 are rejected under 35 U.S.C. 103(a) as being unpatentable over Takahashi (U.S. Patent No. 5,453,137) (Office action point 12).**

The rejection of claims 1-3 and 5-7 under 35 U.S.C. 103(a) is respectfully traversed.

The Examiner indicates that “even if the aluminum phosphate layer of Takahashi does not inherently meet the claimed thickness, one skilled in the art would have found it obvious to adjust

the thickness within the claimed range of 5 to 100 nm.”

Applicants have argued above in regard to the rejection of these claims under 35 U.S.C. 102(b) over Takahashi ‘137 that Takahashi’s permanent magnet does not anticipate the structural limitations of the claims with regard to the location of the rare-earth element. Therefore, even if Takahashi’s coating met the thickness limitations of the present claims, Takahashi still would not provide all of the limitations of the present claims.

Applicants therefore respectfully submit that claims 1-3 and 5-7 are novel and non-obvious over Takahashi ‘137.

**Claims 1-8 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shinichi et al. (JP 2000-058312) (Office action point 13).**

The rejection of claims 1-8 is respectfully traversed.

The Examiner states that in the absence of establishing criticality or unexpected results, one skilled in the art would have found it obvious to adjust Shinichi’s treatment by phosphoric acid, zinc phosphate or phosphoric acid manganese system (paragraph [0014]) to give a phosphate layer having the thickness recited in the claims.

In traversing the rejection, Applicants submit that the present invention as claimed has unexpected results over Shinichi et al.

In Shinichi et al., there is no disclosure with respect to the thickness of the phosphate coating produced by the disclosed treatment. That is, in Shinichi et al., there is no recognition of any importance of the thickness range.

The thickness 5 to 100 nm of the phosphate coating is extremely important in the present invention. The importance of this thickness range is discussed in the specification on page 8, last paragraph, in which it indicates that resistance to weather may not be sufficiently secured at less than 5 nm, and that magnetic and kneading characteristics deteriorate at more than 100 nm. The importance is also apparent from the Examples in the specification. For example, as seen in Table 1 (page 19), Comparative Examples 1, 2 and 4 have coating film thicknesses outside the claimed range. These Comparative Examples clearly have coercive force values after 24 hours that are much lower than the inventive Examples.

As Shinichi does not discuss any effect of the thickness of a phosphate layer produced by the treatment described in paragraph [0014], the effect of the limitation of the thickness of the phosphate film to 5 to 100 nm of the present invention is unexpected over Shinichi et al.

**Claims 9-12 are rejected under 35 U.S.C. 103(a) as being unpatentable over Ohashi (EP 0430198) in view of Takahashi and Shinichi et al. (Office action point 14).**

The rejection of claims 9-12 is respectfully traversed.

Ohashi EP'198 discloses providing the surface of a Nd-Fe-B magnet with a surface coating film of a material having corrosion resistance, for example by electrolytic or electroless nickel plating, aluminum ion-chromating, spray coating of an epoxy resin, electrodeposition of an epoxy resin, and the like (page 2, lines 27-30). The coating film may be formed following a pretreatment with zinc phosphate (page 3, lines 2-3). When nickel plating, the thickness of the nickel layer is 8 to 20  $\mu\text{m}$  and the entire coating including an epoxy resin and the undercoating of zinc phosphate is 10 to 30



$\mu\text{m}$  (page 4, lines 32-33).

The disclosed magnet has a sintered body made of fine particles having an average diameter of 3 to 5  $\mu\text{m}$  (column 4, line 50), which are compression molded and sintered to give an anisotropic sintered permanent magnet. In Example 1 on page 5, the reference discloses preparation of a sintered magnet which is worked into a disc having a diameter of 20 mm and an thickness of 1.5 mm. This magnet was pretreated (line 22) in an unspecified manner, followed by electrolytic nickel plating. The thickness of the nickel film may be 10 to 30  $\mu\text{m}$  (page 7, line 46).

In traversing the rejection, Applicants note first of all that EP'198 discloses pretreatment of a "Nd-Fe-B magnet" with a zinc phosphate coating, but this magnet cannot be considered to be a "magnet powder". Rather, the magnet in EP'198 is clearly much larger than typical powders, and in fact may be made of sintered powders. The powders themselves are not pretreated with the zinc phosphate.

Moreover, in EP'198, the pretreatment with zinc phosphate is not described in detail, and the thickness of the "undercoating of zinc phosphate" is not specified. Applicants submit that the thickness of the "undercoating" cannot be discerned from page 4, lines 32-33 of the reference.

Applicants also note that, based on page 5, lines 22-24, of the reference, after pretreatment (presumably with zinc phosphate), the magnet is treated by alkali degreasing, washing with water, neutralization, washing with water, acid washing and washing with water again. Applicants submit that it is unclear as to how much zinc phosphate could remain after this. Applicants therefore assert that there is no suggestion in the reference for a phosphate film of 5 to 100 nm following this treatment.

Amendment under 37 CFR 1.111  
Kenji OHMORI et al.

U.S. Patent Application Serial No. 09/963,674  
Attorney Docket No. 011020

Applicants therefore submit that claims 9-12 are novel and non-obvious over Ohashi, Shinichi and Takahashi et al., taken separately or in combination.

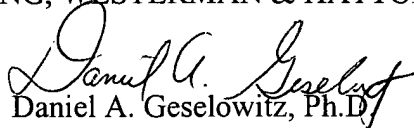
If, for any reason, it is felt that this application is not now in condition for allowance, the Examiner is requested to contact Applicants undersigned agent at the telephone number indicated below to arrange for an interview to expedite the disposition of this case.

Attached hereto is a marked-up version of the changes made by the current amendment. The attached page is captioned "Version with markings to show changes made."

In the event that this paper is not timely filed, Applicants respectfully petition for an appropriate extension of time. Please charge any fees for such an extension of time and any other fees which may be due with respect to this paper, to Deposit Account No. 01-2340.

Respectfully submitted,

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE CLAIMS:**

Please amend 1-8 and 10 claims as follows:

1. (Amended) A highly weather-resistant ~~iron-based~~ magnet powder comprising iron and a rare-earth element, wherein particles of said magnet powder comprise uniform coating with a phosphate film to a thickness of 5 to 100 nm on the average.

2. (Amended) The highly weather-resistant magnet powder according to Claim 1, wherein said ~~iron-based~~ magnet powder comprising iron and a rare earth element is an alloy powder selected from the group consisting of ~~Nd-Fe-B-based~~ Nd-Fe-B and ~~Sm-Fe-N-based~~ Sm-Fe-N powder.

3. (Amended) The highly weather-resistant magnet powder according to Claim 2, wherein the particles of said ~~Sm-Fe-N-based~~ Sm-Fe-N alloy powder are uniformly coated with a zinc film before being coated with said phosphate film.

4. (Amended) The highly weather-resistant magnet powder according to Claim 1, wherein said phosphate coating film is a composite composed of iron phosphate and another phosphate and comprises iron phosphate in an Fe/rare earth element atomic ratio of 8 or more.

5. (Amended) A resin composition for bonded magnets, comprising, as the ~~main~~ ingredient present in the largest amount by weight, ~~the~~ a highly weather-resistant magnet powder comprising a rare-earth element, wherein particles of said magnet powder comprise uniform coating with a

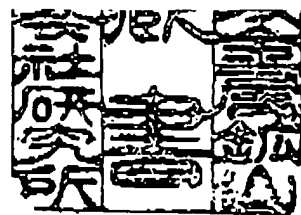
phosphate film to a thickness of 5 to 100 nm on the average.

6. (Amended) The resin composition for bonded magnets according to Claim 5, wherein said ~~iron-based~~ magnet powder comprising iron and a rare earth element is an alloy powder selected from the group consisting of ~~Nd-Fe-B-based~~ Nd-Fe-B and ~~Sm-Fe-N-based~~ Sm-Fe-N powder.

7. (Amended) The resin composition for bonded magnets according to Claim 6, wherein the particles of said ~~Sm-Fe-N-based~~ Sm-Fe-N alloy powder are uniformly coated with a zinc film before being coated with said phosphate film.

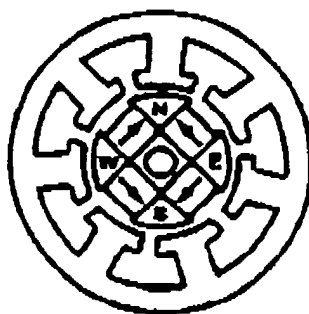
8. (Amended) The resin composition for bonded magnets according to Claim 5, wherein said phosphate coating film is a composite composed of iron phosphate and another phosphate and comprises iron phosphate in an Fe/rare earth element atomic ratio of 8 or more.

10. (Amended) The highly weather-resistant iron-based magnet powder according to claim ~~4~~ 4, wherein the magnet powder is formed as a compacted magnet by compacting the highly weather-resistant magnet powder to an apparent density of 85% or more of the intrinsic density.



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## The effect of Co and Zr substitutions on the magnetic properties of nanostructured Didymium (Nd-Pr)-Fe-B alloys.

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The influence of composition on the grain size distribution and magnetic properties (including exchange enhancement) of several series of nanostructured as-melt spun Didymium (Nd-Pr)-Fe-B based alloys has been investigated. The systems studied include (i) stoichiometric 2/14/1 alloys with various Nd:Pr ratios and with 20 % substitution of Co for Fe or 1 at% substitution of Zr for Fe, (ii) off-stoichiometric ( $\text{Pr}_{0.25}\text{Nd}_{0.75}$ )-Fe-B alloys with 20% Co or 1at%Zr substitution for Fe and with various RE:Fe ratios. For the Co substituted alloys, excellent enhancement of remanence ( $J_r$ ) to values up to 1.15 T for the stoichiometric composition and up to 1.21 T for sub-stoichiometric alloys, was attained. This resulted in attractive values of energy product  $(\text{BH})_{\text{max}}$ , in the range 150-180 kJ/m<sup>3</sup> and with substantially increased Curie temperature  $T_c$  (up to 460 °C) but without serious decrease of  $H_c$  (relative to the Co-free samples). For the Zr-containing samples in the stoichiometric regime, a large increase of 50% in  $H_c$  (up to ~1100 kA/m) was observed, while retaining good  $J_r$  and  $(\text{BH})_{\text{max}}$  values (0.97-0.99 T and 160-180 kJ/m<sup>3</sup>, respectively). For the off-stoichiometric Zr-containing alloys, good remanence values were preserved (0.92 T-1.14 T) and, owing to the improved loop shapes obtained, higher  $(\text{BH})_{\text{max}}$  were also observed (142-163 kJ/m<sup>3</sup>). Enhanced  $H_c$  relative to the Zr free samples within the range 480-1320 kA/m, were also attained. The effects on the magnetic properties are discussed in terms of the influence of the Nd:Pr ratio and of Co and Zr on the intrinsic magnetic properties and on the grain size distributions.

### INTRODUCTION.

The substitution of Nd by Pr in nanostructured  $\text{RE}_2\text{Fe}_{14}\text{B}$  hard magnetics alloys is of interest because the anisotropy field  $H_A$ , and thus the intrinsic coercivity  $H_c$ , are increased which at least partly compensates for the attenuation of  $H_c$  associated with inter-granular exchange coupling in the nanoscale grains. Previous work has shown the effects and usefulness of such substitution [1-3].

An important disadvantage of commercial NdFeB magnets is their low Curie temperature, which limits their technological applications. However, it is well known that Co substitution for Fe in REFeB alloys increases the Curie temperature  $T_c$  [4-8] which is also useful in compensating for  $T_c$  reduction associated with the addition of Pr. In addition, Co substitution for Fe has been reported to increase the saturation magnetisation of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase [6, 9] and thus, higher  $J_r$  and better  $(\text{BH})_{\text{max}}$  values would be expected. Also Zr additions are known to promote, in some circumstances, grain refinement and improved loop shape and coercivity [8, 10, 11]. In this paper, the effects of the addition of both Co and Zr on the magnetic properties and thermal stability of Didymium (Nd+Pr)-Fe-B alloys are presented and discussed.

# High-Performance Nanocrystalline $\text{PrFeB}$ -Based Bonded Permanent Magnets

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## Abstract

Investigations of the magnetic properties of nanocrystalline exchange-coupled  $\text{Pr}_2\text{Fe}_{14}\text{B}$  single-phase and  $\text{Pr}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$  two-phase bonded permanent magnets are reported. For manufacturing the samples, at first nanocrystalline ribbons showing a significant enhancement of the remanence were produced using the melt-spinning technique by direct quenching into the nanocrystalline state. The melt-spun ribbons were powderized (particle size  $1 - 40 \mu\text{m}$ ) and then industrially fabricated into isotropic polymer bonded magnets (density  $6.0 \text{ g/cm}^3$ ). For the polymer bonded magnets the magnetic properties are determined in the temperature range  $T \leq 200^\circ\text{C}$  and compared with the corresponding ribbon material. The best  $(BH)_{\text{max}}$  values obtained at room temperature for our bonded composite magnets containing 30.4 vol%  $\alpha\text{-Fe}$  are in the order of  $90 \text{ kJ/m}^3$  compared to  $180 \text{ kJ/m}^3$  for the ribbons. From the temperature dependence of the coercive field the microstructural parameters  $N_{\text{eff}}$ ,  $\alpha_K$  and  $\alpha_{\text{ex}}$  are determined within the framework of the nucleation model describing the influence of the non-ideal microstructure and the effect of the exchange coupling on the coercive field. Using a simple micromagnetic model the exchange coupling between two adjacent grains is described on the basis of micromagnetism. In analogy to a domain wall, analytical expressions are derived for the remanence enhancement and the approach to saturation. The model calculations can be considered as a first step of a theoretical derivation of the microstructural parameter  $\alpha_{\text{ex}}$ .

## Introduction

Nanocrystalline magnetic materials based on  $\text{RE}_2\text{Fe}_{14}\text{B}$  ( $\text{RE} = \text{Nd, Pr}$ ) have opened a new class of permanent magnet materials which may be well-suited for high-performance isotropic bonded magnets.

Nanocrystalline materials in general are isotropic concerning the distribution of easy axis in the nanoscaled magnetic grains. The most common way for producing high-quality nanocrystalline permanent magnets (pms) is the melt-spinning technique. On the basis of the ternary  $\text{RE-Fe-B}$  phase diagram three types of nanocrystalline pms can be tailored. Firstly, magnets with RE-excess (conventional decoupled magnets) where the hard magnetic  $\text{RE}_2\text{Fe}_{14}\text{B}$  grains are separated by a paramagnetic RE-rich intergranular film limiting the remanence to  $J_R \leq 0.5J_S$  ( $J_S(\text{Nd}_2\text{Fe}_{14}\text{B}) = 1.60 \text{ T}$ ,  $J_S(\text{Pr}_2\text{Fe}_{14}\text{B}) = 1.56 \text{ T}$ , spontaneous polarization). Secondly, stoichiometric magnets [1-3] where the hard magnetic grains are exchange coupled as they are in direct contact leading to an enhancement of the remanence ( $J_R > 0.5J_S$ ) provided that the average grain size is smaller than  $50 \text{ nm}$  [4]. Thirdly, composite magnets [2,3,5-8] where overstoichiometric  $\alpha\text{-Fe}$  increases the remanence further by its large spontaneous polarization ( $J_S = 2.15 \text{ T}$ ) as well as by exchange coupling between the grains provided that the grain size of the soft magnetic grains is in the order of the Bloch wall width  $\delta_B$  of the hard magnetic phase [9]. Especially the composite magnets are optimally suitable for the fabrication of polymer bonded magnets, i.e. the embedding of the powderized nanocrystalline material in a nonmagnetic matrix of epoxy resin, due to their high  $(BH)_{\text{max}}$  values ( $(BH)_{\text{max}} \leq J_R^2/(4\mu_0)$ ) and their low RE content compared to conventional magnets which reduces the cost of the raw materials and improves the corrosion resistance. With bonded magnets any final shape can be prepared easily without expensive after-treatment like sawing or grinding. Moreover, such magnets are characterized by low brittleness, low electric conductivity and by their isotropy which is needed for multipole applications. However, the major drawback to bonded magnets is the reduction in their magnetic properties relative to their fully dense counterpart. This reduction can be estimated with the so-called filling factor  $f$  which reflects



## Nanostructure Formation in Mechanically Milled Nd-Fe-B Alloys

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### Abstract

Mechanical milling of ingot Nd-Fe-B alloys, followed by diffusion annealing has been employed for the processing of nanostructured permanent magnet materials. Three alloys, having total rare earth metals (RE) contents of 13.5 at% Nd, 18 at% Nd and 18 at% Nd+Dy, were investigated. The milling times varied from 0 to 100 h. The effect of annealing temperatures in the range of 530 – 850 °C was also investigated for each composition. It was found that even 5 h milling time, followed by annealing, produced coercive material. Longer milling times did not change substantially either the coercivity or the remanence. However, the compacts which were pressed in a magnetic field from powders milled for times between 5 and 40 h exhibited some degree of anisotropy. For the Nd<sub>13.5</sub>Fe<sub>79.5</sub>Si<sub>1</sub>B<sub>4</sub> sample prepared in this way a (BH)<sub>max</sub> value of 118 kJ/m<sup>3</sup> was obtained. The samples produced from powder milled for longer times were fully isotropic. Annealing at 550 °C for 30 min. produced the best combination of magnetic properties for the two 18 at% RE alloys while an anneal at 650 °C produced the best combination for the 13.5 at% Nd alloy.

### Introduction

Application of mechanical alloying (MA) and mechanical milling (MM), for the processing of nanocrystalline permanent magnets has been extensively studied over the last decade [e.g. 1-6]. These methods have proved to be a useful way of producing such fine grained materials and are broadly competitive, in terms of properties achieved, with the widely used melt spinning route [7,8]. MA and MM, which are processes for high energy ball milling of elementary powders and crushed alloys, respectively, have shown to be especially suitable for the production of exchange coupled magnetic nanocomposites Nd<sub>2</sub>Fe<sub>14</sub>B -  $\alpha$ Fe and Sm<sub>2</sub>Fe<sub>17</sub>N<sub>3</sub> -  $\alpha$ Fe [e.g. 3-6]. The formation of nanostructured materials for these alloys occurs by controlled crystallisation of amorphous material produced by ball milling. Apart from the Nd-Fe-B and Sm-Fe-N systems, MM has also been successfully applied for the processing of Nd<sub>2</sub>Fe<sub>14</sub>B - Fe<sub>3</sub>B magnets [9]. The nanoscale grain size is particularly important for the low RE containing magnets for which a highly refined hard/soft composite structure leads to additional enhanced remanence, with a favourable J-H loop shape and correspondingly high maximum energy product, (BH)<sub>max</sub> [8,10].

In the present study mechanical milling was applied for the processing of nanocrystalline "superstoichiometric" RE-Fe-B alloys with RE contents ranging from 13 at% up to 18 at%. The aim of the investigation was to study microstructural refinement during the course of milling and to establish whether it is possible to align the nanoscale grains before the material is amorphised. The magnetic properties were also measured and the results are discussed in terms of the microstructural changes.

## Characteristics of Epoxy Resin Bonded Magnets Prepared from Recycled Nd-Fe-B Based Melt-Spun Powder.

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### Abstract

Epoxy resin is generally used as binder for consolidating Nd-Fe-B melt-spun powder into a specific shape, because the usage of this binder enables us to obtain a density higher than that of other polymers. However, the reports concerning the method of recycling melt-spun powder included in epoxy resin-bonded magnets are few. Thus, we newly developed a technique for recycling Nd-Fe-B melt-spun powder using the liquid phase pyrolysis of cured epoxy in solvent, and prepared Nd-Fe-B bonded magnets using the recycled powder. This contribution reports the newly developed technique for recycling Nd-Fe-B melt-spun powder, evaluates magnetic properties of the bonded magnets prepared from the recycled melt-spun powder, and compares the proposed method with other recycling methods.

### Introduction

The market of Nd-Fe-B bonded magnets has experienced the fastest growth of permanent magnet markets. Nd-Fe-B melt-spun powder is widely used in the magnet industry as a material for Nd-Fe-B bonded magnets, and all the powder is manufactured by the melt-spinning although other techniques such as atomization are being investigated. As the melt-spun powder generally has isotropic nature due to the nature of quenching process[1], activities in developing applications of Nd-Fe-B bonded magnets have been focussed on high-performance small magnet motors. In preparation of Nd-Fe-B bonded magnets, epoxy resin is widely used as binder for consolidating Nd-Fe-B melt-spun powder into a specific shape, because the usage of this binder enables us to obtain magnets with a density higher than that of other polymers.[2]-[6]

Considering the fast increase in production of Nd-Fe-B bonded magnets, the zero-emission policy may be applied to the bonded magnets in near future in term of the environment protection. Therefore, development of a recycling technique of epoxy resin-bonded magnets is necessary.

Thus, we newly developed a technique for recycling melt-spun powder using liquid phase pyrolysis of cured epoxy resin [7], and prepared bonded magnet from the recycled powder. For all kinds of melt-spun powder studied, coercivity and remanence of recycled magnets were almost the same with those of the corresponding magnets before the recycling. This contribution reports the newly developed method, evaluates magnetic properties of the recycled magnets, and compares them with those obtained by other recycling methods.

### Experiment

#### *A. Melt-spun powders for experiment*

Five kinds of Nd-Fe-B based melt-spun powder with different alloy compositions including  $\alpha$  Fe/Nd-Fe-B based nano-composite melt-spun powder ( $\text{Nd}_{1.8}\text{Fe}_{65}\text{Co}_{16}\text{B}_6$ ,  $\text{Nd}_{12.5}\text{Fe}_{75.5}\text{Co}_5\text{B}_6\text{Nb}_1$ ,  $\text{Nd}_{12}\text{Fe}_{77}\text{Co}_5\text{B}_6$ ,  $\text{Nd}_{10.5}\text{Fe}_{80.5}\text{Co}_3\text{B}_6$ ,  $\text{Nd}_4\text{Fe}_{88}\text{B}_6$ ) were used for preparing epoxy resin-bonded

## The Production and Characterisation of Highly Anisotropic PrFeCoB-type HDDR Powders.

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A study of the processing of highly anisotropic HDDR powder and PTFE-bonded magnets with the composition  $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{M}_{0.1}$  ( $\text{M} = \text{Zr}$  or  $\text{Nb}$ ) has been undertaken. These alloys were processed by an homogenising heat treatment for a range of times, and a subsequent HDDR treatment employing a range of disproportionation times. The optimum time for the homogenisation of the as-cast structure was found to be 20 hours at  $1100^\circ\text{C}$ , while the optimum disproportionation time in the HDDR treatment was found to be 10 minutes at  $860^\circ\text{C}$ . Zr-additions appear to inhibit grain growth during the heat treatment process, whereas Nb-additions appeared to control more effectively the grain growth during the disproportionation and recombination stages of the HDDR process.

### 1. Introduction.

For the last 10 years, Hydrogenation Disproportionation Desorption and Recombination (HDDR) processing of Nd-Fe-B-based alloys has received extensive attention [see for example 1,2]. This possible alternative to the melt spun processing route for bonded permanent magnets has been detailed in a recent review [3]. Recently, studies have also been reported on the HDDR processing of Pr-Fe-B-type alloys [4,5,6]. Thus, a HDDR processed  $\text{Pr}_{13}\text{Fe}_{81}\text{B}_6$  alloy was reported to have a remanence ( $B_r$ ) of 670 mT and an intrinsic coercivity ( $iH_c$ ) of 549 kA/m [4]. More recent work [6,7] reported a  $B_r$  of 1000 mT and an  $iH_c$  of 732 kA/m for a HDDR powder based on the alloy  $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{Zr}_{0.1}$ . The growing interest in Pr-Fe-B-type alloys, with regard to the HDDR process, is related to the Pr-based sintered magnets appearing to have a different grain growth behaviour in comparison with that of Nd-based systems [8], and this could lead to a greater control of the grain growth during and after the recombination stage.

In the present work, an investigation of HDDR powder based on the alloys  $\text{Pr}_{13.7}\text{Fe}_{63.5}\text{Co}_{16.7}\text{B}_6\text{M}_{0.1}$  ( $\text{M} = \text{Zr}$  or  $\text{Nb}$ ) has been carried out. PTFE-bonded magnets have subsequently been produced from the powders using an uniaxial pressing technique. In order to achieve the best magnetic properties, the processing of the magnetic material was optimised for both the heat treatment time at  $1100^\circ\text{C}$  and the HDDR conditions (in particular, the dwell time of the disproportionation stage). The evolution of the microstructure with time at  $1100^\circ\text{C}$  was investigated by means of a SEM study to correlate with the variation of the magnetic properties.

### 2. Experimental.

The alloys investigated in this work have been provided by Rare Earth Products Ltd. (Honeywell), Widnes, UK. The samples (as received), were crushed coarsely into pieces ( $1\text{--}2\text{ cm}^3$ ) and then homogenised with a heat treatment under vacuum ( $10^{-1}$  mbar) at  $1100^\circ\text{C}$  for a range of times. The heat treated material was then crushed into finer lumps ( $5\text{--}10\text{ mm}^3$ ) and 15g batches were placed into a HDDR reactor and treated with the processing parameters optimised

# Structure Changes in $\text{Sm}_2\text{Fe}_{17}$ -based Permanent Magnet Materials Induced by HDDR Process

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## Abstract

Besides the matrix grain sizes of  $\text{Sm}_2\text{Fe}_{17}$ -based materials becoming small ( $0.2\ \mu\text{m}$ ), the crystal structure change from the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure to the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure is observed after the HDDR process. In the  $\text{Sm}_2\text{Fe}_{17}$  alloy, during the HD process,  $\text{SmH}_2$  fibers with about  $7\ \text{nm}$  in diameter and  $1\ \mu\text{m}$  in length are arrayed in a nearly regular arrangement with an average distance of  $11\ \text{nm}$  in the  $\alpha\text{-Fe}$  matrix. All the  $\text{SmH}_2$  fibers have the same orientation and grow with definite orientation relationships to the  $\alpha\text{-Fe}$  matrix i.e.,  $\{100\}\text{SmH}_2 // \{100\}\alpha\text{-Fe}$  and  $\langle 001 \rangle \text{SmH}_2 // \langle 001 \rangle \alpha\text{-Fe}$ . During the DR process, it seems that the  $\text{SmH}_2$  fibers firstly break into small spheres and then several of these spheres combine into a bigger one before recombining with the  $\alpha\text{-Fe}$  grains. In a  $\text{Sm}_{4.3}\text{Fe}_{24.3}\text{B}_{2.0}\text{Ti}_{1.8}$  alloy, the disproportionation reaction initiates from grain boundaries. However,  $\text{SmH}_2$  grains do not change to spherical grains during the DR process. During the DR process after the incomplete HD process, there is a certain orientation relationship between the recombined submicron grains and the undisproportionated matrix.

## Introduction

The interstitially modified nitride  $\text{Sm}_2\text{Fe}_{17}\text{N}_2$  has been considered as a promising candidate for permanent magnet applications because of its excellent intrinsic magnetic properties, such as Curie temperature, saturation magnetization and magnetic anisotropy field, which are comparable to or better than those of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase. Therefore, the  $\text{Sm}_2\text{Fe}_{17}$ -nitride-based permanent magnets have the potential surpassing  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based permanent magnets, which are presently considered to be the best. In the light of this prospect, worldwide efforts have been devoted to the improvement of the hard magnetic properties of  $\text{Sm}_2\text{Fe}_{17}\text{N}_2$  since its emergence in 1990 [1-3]. Recently, the hydrogenation-disproportionation-desorption-recombination (HDDR) process, which is known to be an enticing process to produce rare earth alloy permanent magnet powders with a large energy product [4-7] and an effective method for obtaining highly coercive by changing originally coarse grained material to recombine into fine grains (typical grain size:  $\sim 0.3\ \mu\text{m}$ ), has been attracting much attention [8-9]. Without the HDDR process, unmilled  $\text{Sm}_2\text{Fe}_{17}\text{N}_2$  powder has a coercivity of approximately  $1\ \text{kOe}$  [10]. When nitrogeneration follows the HDDR process, the coercivity is improved to  $17\ \text{kOe}$  [11]. The idea behind the above-mentioned method is to develop a suitable microstructure that is favorable for generating hard magnetic properties from the powders. The HDDR process is completed by the heat treatment in hydrogen and further treatment in vacuum [12]. The original compound disproportionates into a rare-earth metal hydride and  $\alpha\text{-Fe}$  grains by hydrogenation, and then rare-earth metal hydride and  $\alpha\text{-Fe}$  grains recombine to the original structure but with fine grains by the treatment in vacuum. Thus, the microstructures after the hydrogenation-disproportionation (HD) and the desorption-recombination (DR) processes are important to control the final structures, which strongly influence permanent magnetic properties.

Recently, magnetic materials with high magnetic coercivity in the  $\text{Sm-Fe-B-Ti}$  alloys prepared by the HDDR process followed by a nitridation have been obtained [13]. The purpose of this work is to investigate the structures of the  $\text{Sm}_2\text{Fe}_{17}$ -based alloys during the HDDR process.

## Procedure